A DESCRIPTION OF EFFECT OF COMPOSITION OF MIXED BINARY SOLVENTS ON PROCESSES IN SOLUTIONS

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A theoretical description of the effect of changed composition of mixed solvents on processes in solutions has been suggested on the basis of the proportionality between the Gibbs energy change of the process and that of the solvent due to the transition from pure components to the mixture. The additional Gibbs energy has been expressed by means of the so-called classical functions by Margules, van Laar–Wohl, and van Laar–Null. The application to 115 various processes (pK, IR, UV-VIS, NMR, log k, and others) has confirmed that the theoretical presumptions are justified, the most suitable being Margules' 4th order model which shows a statistically significant difference from the models of lower orders.

Although from practical point of view solvent mixtures are more important than one-component solvents, the effects of solvents mixtures on various processes in solutions are less investigated. This fact is obviously caused by greater complexity and diversity of the problem, as in addition to the effect itself (i.e. that of the solvent on the process) mutual interactions of the solvent components are also important, which leads to non-additivity of the effect and behaviour of the mixture.

The most frequent approach to evaluation of effects of mixed solvents on processes in solutions is based on applications of functions of relative permittivity and refractive index (e.g. refs[1–9]). The drawbacks of these models are revealed by measurements in "isodielectric" mixtures[10,11] which indicate further types of interactions. One of the approaches even applies the description of the dependence of logarithm of rate constant on logarithm of water concentration in hydrolytical reactions[12–18], which is an often misleading oversimplification. A more successful application of this approach is based on the behaviour (of rate constants in this case) in one-component solvents which, according to the ideas about the existence of solvates, is decisive for a prediction of the behaviour in mixtures[19–21]. Empirical procedures based on applications of extrathermodynamic relations already have their tradition based on the Y parameter[22]. This concept was developed later with application of other standard substrates[8,9,23–29]. The applicability of these parameters was increased by the suitable transformation[30] which leads to a linear dependence of the result of a process on the empirical parameters within the whole concentration range of the

components in a mixed solvent. While the choice of the standard model is critical for these empirical relations, the empirical relations for multicomponent mixtures suffer from an additional disadvantage consisting in the vast number of combinations of components and compositions which can be neither measured nor tabulated. From this point of view more practical are the ways of interpretation based on the properties of the pure components with the help of relations which can suitably approximate the behaviour of solutes depending on the solvent composition. Although these are often non-linear dependences with several parameters (which need a greater number of experimental points), they are advantageous in being more general and allowing the interpretation of the parameter values obtained.

The aim of this work is to suggest and verify a relation for description of effects of mixed solvents on processes in solutions on the basis of physico-chemical ideas with application of the expansions for the additional Gibbs' function.

THEORETICAL

Any physical or chemical process in a solution can be described as a function of the Gibbs energy difference between the initial and final states. As there always are substantially less molecules undergoing a process in the solution than the solvent molecules, the effect of the process on the solvent as a whole can be — in the first approximation — neglected. If the process taking place in the solution is taken as one system and the solvent as the other system, then the difference between the chemical potentials "after the process" and "before the process" can be considered proportional to that of solvent, α being the coefficient of proportionality (sensitivity)

$$\mu^{\text{after}} - \mu^{\text{before}} = \alpha \cdot \mu^{\text{solv.}} \ . \tag{1}$$

According to the definition the chemical potential is the change of the Gibbs energy with the change of the number of mol at constant pressure and temperature (the superscripts p and s denote the process and solvent, respectively):

$$\partial \, \Delta G^{\text{p}}/\partial n_i = \alpha(\partial G^{\text{s}}/\partial n_i) \ ; \quad p, T = \text{const.} \ ; \quad n_{i \neq j} \ , \tag{2}$$

hence also

$$\mathrm{d}\Delta G^{\text{p}} = \alpha \, \mathrm{d}G^{\text{s}} \ ; \quad p, T = \text{const.} \tag{3}$$

Expressing the total differentials as functions of mol numbers we obtain Eq. (4), where q means number of components.

$$\sum_{i=1}^{q} \left(\partial \, \Delta G^{\text{p}}/\partial n_i \right) \mathrm{d}n_i = \sum_{i=1}^{q} \left(\partial G^{\text{s}}/\partial n_i \right) \mathrm{d}n_i \ ; \quad p, T = \text{const.} \ ; \quad n_{i \neq j} \ . \tag{4}$$

The integration in the sense from pure components to a real mixture gives Eq. (5),

$$\Delta\Delta G^{\mathrm{p}} = \sum_{i=1}^{q} n_i \,\Delta\Delta G_i^{\mathrm{p}} = \alpha \sum_{i=1}^{q} n_i \,\Delta G_i^{\mathrm{s}} = \alpha \,\Delta G^{\mathrm{s}}\,, \tag{5}$$

where $\Delta\Delta G_i^{\mathrm{p}}$ represents the change of ΔG of the process with the change of number of mol on going from the i-th pure solvent to the real mixture, and ΔG_i^{s} means the contribution of the i-th solvent to the Gibbs energy change of formation of the mixture from pure components. If the system is ideal (denoted by asterisk), Eq. (6) can be similarly written

$$\Delta\Delta G^{*\mathrm{p}} = \sum_{i=1}^{q} n_i \,\Delta\Delta G_i^{*\mathrm{p}} = \alpha \sum_{i=1}^{q} n_i \,\Delta G_i^{*\mathrm{s}} + \alpha \,\Delta G^{*\mathrm{s}}\,. \tag{6}$$

With application of Eqs (5) and (6), the difference between ΔG^{p} in a real solution and that in an ideal one can be expressed by Eq. (7) in which ΔG^{E} is the so-called additional change of Gibbs' function

$$\Delta\Delta G^{\mathrm{p}} - \Delta\Delta G^{*\mathrm{p}} = \alpha(\Delta G^{\mathrm{s}} - \Delta G^{*\mathrm{s}}) = \alpha \,\Delta G^{\mathrm{E}}\,. \tag{7}$$

If the solution is an ideal one, it can be anticipated that the effects of the individual components of the solvent on the process taking place therein will be identical with those of the same components in the respective one-component solvents. Then Eq. (8) is valid, and Eq. (7) can be rewritten to the form of Eq. (9) in which $\Delta G_{0i}^{\mathrm{p}}$ are ΔG values in pure components

$$\Delta\Delta G^{*\mathrm{p}} = 0 \tag{8}$$

$$\Delta G^{\mathrm{p}} = \Delta G_0^{\mathrm{p}} + \alpha \,\Delta G^{\mathrm{E}} = \sum_{i=1}^{q} n_i \,\Delta G_{0i}^{\mathrm{p}} + \alpha \,\Delta G^{\mathrm{E}}\,. \tag{9}$$

The ΔG^{p} and $\Delta G_{0i}^{\mathrm{p}}$ values can be expressed by means of $\ln K$ of an equilibrium process, $\ln k$ of a rate process, or some other analogous quantity with the energy/mol dimension.

The additional change of Gibb's function with the composition of liquid phase can be expressed by Wohl's expansion[31] which generalizes a number of equations (Margules[32], Van Laar[33], Null[34], Redlich–Kister[35], and others). Beside these so--called classical equations there are non-classical ones.

In terms of the classical equations and with reference to the overall mol number, Eq. (9) for a binary mixture can be rewritten to the following forms (the superscript for "process" is omitted): the application of the regular[32] for expressing the additional Gibbs function leads to Eq. (10), the expansions of the 3rd and 4th orders (Margules[32]) lead to Eqs (11) and (12), respectively, application of the expansion by van Laar & Wohl[33] gives Eq. (13), whereas that by van Laar and Null[34] leads to Eq. (14).

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 A_{12} \tag{10}$$

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 (x_1 A_{21} + x_2 A_{12}) \tag{11}$$

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 (x_1 A_{21} + x_2 A_{12} - x_1 x_2 D_{12}) \tag{12}$$

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 A_{12} A_{21} / (x_1 A_{12} + x_2 A_{21}) \tag{13}$$

$$\Delta G = x_1 \, \Delta G_{10} + x_2 \, \Delta G_{20} + x_1 x_2 A_{12} A_{21} (x_1 A_{12} + x_2 A_{21}) /$$
$$/(x_1 |A_{12}| + x_2 |A_{21}|)^2 \tag{14}$$

The 3rd order equation by Redlich and Kister[35] is identical with that by Margules (11). In all the equations the proportionality coefficient is included in the parameters.

RESULTS AND DISCUSSION

For testing of applicability of Eqs (10) through (14) to the description of effects of binary mixed solvents on processes in solutions we used 115 examples from literature (Table I). The testing includes data on dissociation constants, NMR, IR and UV-VIS spectra, rate constants, thermodynamical, electrochemical and other quantities. The optimization[104] of the parameters in the models (10) through (14) applied to the data of Table I gave the residual mean squares which are summarized in Table II for the four-parameter Eqs (11), (13), (14) and the five-parameter Eq. (12). As the data used were of various types and experimental qualities, the differences between the models were tested by means of the Friedman method[105]. The testing criterion is defined by Eq. (15),

$$Q = 12 \sum_{j=1}^{k} (\sum_{i=1}^{N} \bar{R}_{ij})^2 / (Nk(k + 1)) - 3N(k + 1), \tag{15}$$

where k means number of the models tested, N means number of the examples tested, and R_{ij} means the order of the j-th model within the i-th example tested. If the hypothesis is valid, the Q criterion for $N \to \infty$ asymptotically involves $\chi^2(k - 1)$ distributions. The application of the criterion (15) to the data of Table II and values of residual mean square (they are not given for the regular (Eq. (10)) because of the small significance of this model) gave the value $Q = 109 \cdot 89$. This value by far exceeds the critical value $\chi^2_{0 \cdot 05}(4) = 9 \cdot 49$, wherefrom it follows that the individual methods differ in the value of residual mean square and, hence, in the quality of interpretation of experimental data. The individual methods can easily be compared according to the average order $\bar{R}$: the Margules 4th order equation (Eq. (12)) $1 \cdot 86$, the van Laar and Null equation (Eq. (14)) $2 \cdot 89$, the Margules 3rd order equation (Eq. (11)) $2 \cdot 94$, the van Laar & Wohl equation (Eq. (13)) $3 \cdot 33$, and the regular (Eq. (10)) $3 \cdot 98$. Hence, it can be stated that addition of one parameter will improve the order by

The processes in mixed binary solvents used for testing the physical models

No.	Substrate, process	Mixture[a]	References
		Acid-base equilibria, pK	
1	Benzoic acid, 25°C	MeOH–W	29, 36–50
2		EtOH–W	29, 40, 50–62
3		DMF–W	63–70
4		DMSO–W	63–65, 71–80
5		Ac–W	68, 70, 71, 81, 82
6		Ac–W[b]	68, 71, 81, 82
7	Acetic acid, 25°C	MeOH–W	29, 40, 47, 49, 51
8		EtOH–W	29, 40, 51, 52, 62, 83
9		DMF–W	63–65, 68, 69, 84, 85
10		DMSO–W	63–65, 72, 80, 84, 86, 87
11		Ac–W	51, 68, 70, 88
12		Ac–W[b]	51, 68, 88
13	Formic acid, 25°C	MeOH–W	29, 40, 49
14		EtOH–W	29, 51, 62
15		DMF–W	29, 69
16	Phenol, 25°C	MeOH–W	29
17		EtOH–W	29
18		DMSO–W	63–65, 80
19	Benzenesulphonamide, 25°C	MeOH–W	89
20		DMF–W	89
21	Oxalic acid, 25°C	EtOH–W	29
22	Malonic acid, 25°C	EtOH–W	29
23	Anion of malon. acid, 25°C	EtOH–W	29
24	Succinic acid, 25°C	EtOH–W	29
25	Anion of succ. acid, 25°C	EtOH–W	29
26	Glutaric acid, 25°C	EtOH–W	29
27	Anion of glut. acid, 25°C	EtOH–W	29
28	Water, 30°C	DMSO–W	90
29	Water, 25°C	DMSO–W	90
30	Water, 20°C	DMSO–W	90
		The complex stability constant pβ_{11}	
31	I$_3^-$	DMSO–W	91
		Spectral behaviour	
32	The B_{KT} parameter characterizing the solvent basicity	FA–MeOH	24
33		Et$_2$O–MeOH	24
34		DMSO–MeOH	24

TABLE I
(Continued)

No.	Substrate, process	Mixture[a]	References
35		AN–MeOH	24
36		Ac–MeOH	24
37		DMF–MeOH	24
38		EA–MeOH	24
39		$CHCl_3$–MeOH	24
40		B–MeOH	24
41		D–MeOH	24
42		W–MeOH	24
43		NM–MeOH	24
44		PC–MeOH	24
45		THF–MeOH	24
46		MeOH–W	8
47		EtOH–W	8
48		1-PrOH–W	8
49		2-PrOH–W	8
50		AN–W	8
51		DMSO–W	8
52		DMF–W	8
53		Ac–W	8
54		THF–W	8
55		D–W	8
56		EtOH–Hx	8
57	The $E_T(30)$ parameter characterizing the solvent	MeOH–W	8
58		EtOH–W	8
59		1-PrOH–W	8
60		2-PrOH–W	8
61		AN–W	92
62		DMSO–W	9
63		DMF–W	8
64		Ac–W	8
65		THF–W	8
66		D–W	8
67		EtOH–Hx	92
68	$Z-Z$(EtOH) shift of abs. maximum	EtOH–W	93
69		MeOH–W	93
70		Ac–W	93
71		D–W	93
72	Solvatochromic shift	$DMSO–CCl_4$	94
73		DMSO–PhCl	94

TABLE I

(*Continued*)

No.	Substrate, process	Mixture[a]	References
74		DMSO–DCE	94
75		DMSO–DCM	94
76		THF–CCl$_4$	94
77		MeOH–CCl$_4$	94
78		t-BuOH–CCl$_4$	94
79	NMR chem. shift ^{59}Co	CHCl$_3$–CCl$_4$	95
80	$-\delta\,^1$H(H$_2$O) + δ^1 H((CH$_3$)$_3$COH)	AN–W[c]	96
81		AN–W[c]	96
82		AN–W[c]	96
83		AN–W[c]	96
84		AN–W[c]	96
85	$-\delta\,^1$H(CH$_3$CN) + δ^1 H((CH$_3$)$_3$COH)	AN–W[c]	96
86		AN–W[c]	96
87		AN–W[c]	96
88		AN–W[c]	96

Kinetic behaviour, log k

No.	Substrate, process	Mixture[a]	References
89	Y, (CH$_3$)$_3$CCl	EtOH–W	97
91	(C$_2$H$_5$)$_3$N + C$_2$H$_5$I, 293 K	cHx–Ac	4
92	334 K	cHx–Ac	4
93	323 K	cHx–Ac	4
94	(C$_2$H$_5$)$_3$N + C$_2$H$_5$I, 314 K	cHx–Ac	4
95	C$_6$H$_5$SO$_2$OCH(CH$_3$)$_2$, hydrolysis	Ac–W	12
96	p-NO$_2$C$_6$H$_4$SO$_2$CH$_2$OClO$_3$, hydrolysis	tert-BuOH–W	98
97	p-CH$_3$OC$_6$H$_4$COCF$_3$, hydratation	sulfolan–W	99
98	p-CH$_3$OC$_6$H$_4$COCF$_3$, hydratation	sulfolan–W	99

Thermodynamical characteristics, neutralization

No.	Substrate, process	Mixture[a]	References
99	ΔG, benzoic acid	MeOH–W	100
100	ΔH	MeOH–W	100
101	ΔS	MeOH–W	100
102	ΔG	Ac–W	100
103	ΔH	Ac–W	100
104	ΔS	Ac–W	100
105	ΔG, acetic acid	Ac–W	100

Table I

(Continued)

No.	Substrate, process	Mixture[a]	References
106	ΔH	Ac–W	100
107	ΔS	Ac–W	100
108	ΔG	MeOH–W	100
109	ΔH	MeOH–W	100
110	ΔS	MeOH–W	100
	Other processes		
111	Conductivity, HCl	DMSO–W	101
112	Viscosity	DMSO–W	101
113	Diffusion coefficient	MeOH–W	102
114	Diffusion coefficient	MeOH–W	102
115	Solubility, $NaNO_3$	HNO_3–W	103

[a] W water, MeOH methanol, EtOH ethanol, DMF dimethylformamide, DMSO dimethyl sulphoxide, Ac acetone, FA formamide, Et_2O diethyl ether, AN acetonitrile, EA ethyl acetate, B benzene, D 1,4-dioxane, NM nitromethane, PC propylene carbonate, PrOH propanol, PhCl chlorobenzene, DCE 1,2-dichloroethane, DCM dichloromethane, tert-BuOH 2-methyl-2-propanol, cHx cyclohexane; [b] without the pK value in pure acetone; [c] at various concentrations of the added $AgNO_3$.

about 1. If the regular (Eq. (10)) is excluded as a little satisfactory model and the testing is repeated by means of the criterion (15), the value $Q = 52\cdot47$ is obtained. In this case, too, the critical value $\chi^2_{0\cdot05}(3) = 7\cdot81$ is exceeded, hence the models are not comparable. As it is seen from the newly calculated average order $\bar{R}$: the Margules 4th order equation (12) 1·77, the van Laar and Null equation (14) 2·57, the Margules 3rd order equation (11) 2·74, and the van Laar and Wohl equation (13) 2·91, the non-equivalence of the equations is predominantly due to the difference between the four- and five-parameter equations. Hence, the fifth parameter brings a significant improvement of the interpretation of experimental data.

Table III present a survey of applicability of the individual model equations (11) through (14) to various data types. It can be seen that introduction of a further parameter (i.e. application of Eq. (12)) is significant for the descriptions of effects of binary solvents on the dissociation, IR, and UV-VIS spectra, being insignificant for NMR spectra and rate constants of chemical reactions. This result is also reflected in the average orders. As, theoretically, the process type is irrelevant, the result found can be interpreted as a low sensitivity of the given process to the composition changes of binary solvents. Small deviations from ideal behaviour are negligible (within

TABLE II

Residual mean squares of the models (*11*) through (*14*) for the data of Table I

No.	N	Eq. (*11*)	Eq. (*12*)	Eq. (*13*)	Eq. (*14*)
1	50	$3\cdot922\cdot10^{-2}$	$1\cdot807\cdot10^{-2}$	$1\cdot899\cdot10^{-2}$	$1\cdot899\cdot10^{-2}$
2	38	$6\cdot121\cdot10^{-2}$	$4\cdot129\cdot10^{-2}$	$2\cdot783\cdot10^{-1}$	$8\cdot498\cdot10^{-2}$
3	13	$5\cdot014\cdot10^{-2}$	$5\cdot530\cdot10^{-2}$	$9\cdot588\cdot10^{-2}$	$9\cdot796\cdot10^{-2}$
4	24	$1\cdot140\cdot10^{-2}$	$8\cdot492\cdot10^{-3}$	$1\cdot125\cdot10^{-2}$	$1\cdot083\cdot10^{-2}$
5	20	$1\cdot798\cdot10^{-2}$	$1\cdot582\cdot10^{-2}$	$2\cdot927\cdot10^{-2}$	$2\cdot927\cdot10^{-2}$
6	19	$1\cdot602\cdot10^{-2}$	$1\cdot692\cdot10^{-2}$	$2\cdot834\cdot10^{-2}$	$1\cdot653\cdot10^{-2}$
7	40	$4\cdot233\cdot10^{-2}$	$1\cdot526\cdot10^{-2}$	$2\cdot108\cdot10^{-1}$	$1\cdot732\cdot10^{-2}$
8	41	$1\cdot735\cdot10^{-2}$	$6\cdot525\cdot10^{-3}$	$1\cdot105\cdot10^{-2}$	$1\cdot610\cdot10^{-2}$
9	15	$1\cdot609\cdot10^{-1}$	$1\cdot764\cdot10^{-1}$	$1\cdot606\cdot10^{-1}$	$1\cdot631\cdot10^{-1}$
10	23	$4\cdot684\cdot10^{-3}$	$1\cdot485\cdot10^{-3}$	$4\cdot178\cdot10^{-3}$	$4\cdot178\cdot10^{-3}$
11	22	$1\cdot374\cdot10^{-1}$	$6\cdot516\cdot10^{-2}$	$1\cdot436\cdot10^{0}$	$5\cdot604\cdot10^{-1}$
12	21	$4\cdot452\cdot10^{-2}$	$4\cdot730\cdot10^{-2}$	$4\cdot415\cdot10^{-2}$	$4\cdot448\cdot10^{-2}$
13	23	$4\cdot265\cdot10^{-2}$	$2\cdot889\cdot10^{-2}$	$2\cdot534\cdot10^{-1}$	$1\cdot308\cdot10^{-1}$
14	19	$2\cdot716\cdot10^{-2}$	$6\cdot225\cdot10^{-3}$	$3\cdot283\cdot10^{-3}$	$3\cdot283\cdot10^{-3}$
15	9	$6\cdot907\cdot10^{-1}$	$8\cdot348\cdot10^{-1}$	$8\cdot440\cdot10^{-1}$	$8\cdot440\cdot10^{-1}$
16	15	$6\cdot000\cdot10^{-2}$	$2\cdot385\cdot10^{-2}$	$2\cdot699\cdot10^{-2}$	$2\cdot093\cdot10^{-2}$
17	16	$8\cdot259\cdot10^{-2}$	$4\cdot657\cdot10^{-2}$	$6\cdot243\cdot10^{-2}$	$6\cdot243\cdot10^{-2}$
18	13	$2\cdot099\cdot10^{-2}$	$1\cdot896\cdot10^{-2}$	$1\cdot494\cdot10^{-2}$	$1\cdot494\cdot10^{-2}$
19	23	$4\cdot203\cdot10^{-2}$	$3\cdot069\cdot10^{-3}$	$3\cdot432\cdot10^{-1}$	$2\cdot078\cdot10^{-3}$
20	18	$9\cdot757\cdot10^{-3}$	$7\cdot105\cdot10^{-3}$	$5\cdot736\cdot10^{-2}$	$2\cdot629\cdot10^{-2}$
21	10	$2\cdot282\cdot10^{-2}$	$1\cdot991\cdot10^{-2}$	$2\cdot047\cdot10^{-2}$	$2\cdot047\cdot10^{-2}$
22	10	$2\cdot702\cdot10^{-3}$	$1\cdot600\cdot10^{-3}$	$2\cdot113\cdot10^{-3}$	$2\cdot183\cdot10^{-3}$
23	10	$8\cdot838\cdot10^{-2}$	$1\cdot060\cdot10^{-1}$	$9\cdot825\cdot10^{-2}$	$9\cdot825\cdot10^{-2}$
24	13	$2\cdot447\cdot10^{-2}$	$4\cdot906\cdot10^{-3}$	$1\cdot127\cdot10^{-2}$	$1\cdot127\cdot10^{-2}$
25	10	$7\cdot733\cdot10^{-2}$	$9\cdot268\cdot10^{-2}$	$8\cdot350\cdot10^{-2}$	$8\cdot350\cdot10^{-2}$
26	11	$2\cdot349\cdot10^{-2}$	$1\cdot690\cdot10^{-2}$	$2\cdot415\cdot10^{-2}$	$2\cdot415\cdot10^{-2}$
27	11	$5\cdot062\cdot10^{-2}$	$5\cdot029\cdot10^{-2}$	$5\cdot225\cdot10^{-2}$	$5\cdot225\cdot10^{-2}$
28	21	$2\cdot362\cdot10^{-3}$	$1\cdot898\cdot10^{-3}$	$4\cdot426\cdot10^{-3}$	$7\cdot478\cdot10^{-3}$
29	21	$2\cdot504\cdot10^{-3}$	$2\cdot023\cdot10^{-3}$	$3\cdot728\cdot10^{-3}$	$2\cdot714\cdot10^{-3}$
30	21	$3\cdot225\cdot10^{-3}$	$2\cdot834\cdot10^{-3}$	$3\cdot719\cdot10^{-1}$	$3\cdot719\cdot10^{-2}$
31	12	$3\cdot794\cdot10^{-3}$	$1\cdot764\cdot10^{-3}$	$1\cdot296\cdot10^{-1}$	$1\cdot530\cdot10^{-2}$
32	11	$2\cdot123\cdot10^{-5}$	$1\cdot165\cdot10^{-5}$	$1\cdot427\cdot10^{-4}$	$5\cdot432\cdot10^{-5}$
33	11	$6\cdot718\cdot10^{-5}$	$6\cdot992\cdot10^{-6}$	$4\cdot958\cdot10^{-5}$	$4\cdot958\cdot10^{-5}$
34	11	$2\cdot797\cdot10^{-5}$	$4\cdot429\cdot10^{-6}$	$4\cdot868\cdot10^{-5}$	$4\cdot868\cdot10^{-5}$
35	11	$1\cdot069\cdot10^{-5}$	$7\cdot751\cdot10^{-6}$	$9\cdot993\cdot10^{-5}$	$3\cdot308\cdot10^{-5}$
36	11	$1\cdot054\cdot10^{-5}$	$1\cdot084\cdot10^{-5}$	$3\cdot567\cdot10^{-5}$	$3\cdot567\cdot10^{-5}$
37	11	$4\cdot128\cdot10^{-6}$	$4\cdot759\cdot10^{-6}$	$5\cdot035\cdot10^{-6}$	$5\cdot035\cdot10^{-6}$
38	11	$3\cdot281\cdot10^{-5}$	$1\cdot259\cdot10^{-5}$	$3\cdot308\cdot10^{-5}$	$3\cdot308\cdot10^{-5}$
39	11	$6\cdot902\cdot10^{-4}$	$1\cdot870\cdot10^{-4}$	$6\cdot968\cdot10^{-4}$	$6\cdot968\cdot10^{-4}$
40	11	$8\cdot417\cdot10^{-4}$	$4\cdot224\cdot10^{-4}$	$1\cdot171\cdot10^{-4}$	$1\cdot771\cdot10^{-4}$
41	11	$2\cdot723\cdot10^{-4}$	$7\cdot907\cdot10^{-5}$	$1\cdot390\cdot10^{-5}$	$1\cdot390\cdot10^{-5}$

TABLE II
(*Continued*)

No.	N	Eq. (*11*)	Eq. (*12*)	Eq. (*13*)	Eq. (*14*)
42	11	$3.291 \cdot 10^{-4}$	$2.011 \cdot 10^{-4}$	$3.553 \cdot 10^{-4}$	$3.553 \cdot 10^{-4}$
43	11	$2.843 \cdot 10^{-5}$	$2.611 \cdot 10^{-5}$	$1.068 \cdot 10^{-3}$	$3.196 \cdot 10^{-5}$
44	11	$2.363 \cdot 10^{-5}$	$1.265 \cdot 10^{-5}$	$5.403 \cdot 10^{-4}$	$2.745 \cdot 10^{-5}$
45	11	$4.046 \cdot 10^{-5}$	$1.638 \cdot 10^{-5}$	$1.337 \cdot 10^{-5}$	$1.337 \cdot 10^{-5}$
46	11	$3.944 \cdot 10^{-4}$	$2.063 \cdot 10^{-4}$	$5.602 \cdot 10^{-4}$	$5.602 \cdot 10^{-4}$
47	11	$6.668 \cdot 10^{-4}$	$6.798 \cdot 10^{-4}$	$8.753 \cdot 10^{-4}$	$8.753 \cdot 10^{-4}$
48	11	$2.272 \cdot 10^{-3}$	$1.142 \cdot 10^{-3}$	$2.697 \cdot 10^{-4}$	$2.697 \cdot 10^{-4}$
49	11	$1.790 \cdot 10^{-3}$	$1.997 \cdot 10^{-4}$	$2.103 \cdot 10^{-4}$	$2.103 \cdot 10^{-4}$
50	11	$8.302 \cdot 10^{-4}$	$1.709 \cdot 10^{-4}$	$3.449 \cdot 10^{-4}$	$3.449 \cdot 10^{-4}$
51	11	$6.411 \cdot 10^{-4}$	$9.324 \cdot 10^{-5}$	$5.142 \cdot 10^{-4}$	$5.142 \cdot 10^{-4}$
52	11	$3.719 \cdot 10^{-4}$	$2.171 \cdot 10^{-4}$	$8.083 \cdot 10^{-5}$	$8.083 \cdot 10^{-5}$
53	11	$6.540 \cdot 10^{-4}$	$4.935 \cdot 10^{-4}$	$1.642 \cdot 10^{-4}$	$1.642 \cdot 10^{-4}$
54	11	$5.593 \cdot 10^{-3}$	$2.339 \cdot 10^{-3}$	$3.218 \cdot 10^{-3}$	$5.404 \cdot 10^{-3}$
55	11	$6.548 \cdot 10^{-4}$	$3.023 \cdot 10^{-4}$	$1.080 \cdot 10^{-3}$	$5.588 \cdot 10^{-4}$
56	12	$3.003 \cdot 10^{-3}$	$4.038 \cdot 10^{-4}$	$5.477 \cdot 10^{-4}$	$5.477 \cdot 10^{-4}$
57	11	$3.674 \cdot 10^{-5}$	$1.204 \cdot 10^{-5}$	$1.080 \cdot 10^{-3}$	$2.239 \cdot 10^{-5}$
58	11	$2.176 \cdot 10^{-4}$	$2.261 \cdot 10^{-5}$	$3.281 \cdot 10^{-3}$	$1.271 \cdot 10^{-3}$
59	11	$1.650 \cdot 10^{-3}$	$6.664 \cdot 10^{-4}$	$1.163 \cdot 10^{-5}$	$1.117 \cdot 10^{-5}$
60	11	$1.004 \cdot 10^{-3}$	$2.310 \cdot 10^{-4}$	$5.095 \cdot 10^{-5}$	$4.424 \cdot 10^{-5}$
61	11	$3.840 \cdot 10^{-4}$	$2.558 \cdot 10^{-4}$	$1.161 \cdot 10^{-3}$	$1.161 \cdot 10^{-3}$
62	11	$1.031 \cdot 10^{-4}$	$3.170 \cdot 10^{-5}$	$3.143 \cdot 10^{-3}$	$6.512 \cdot 10^{-5}$
63	11	$2.238 \cdot 10^{-4}$	$3.714 \cdot 10^{-5}$	$3.377 \cdot 10^{-5}$	$2.550 \cdot 10^{-5}$
64	11	$3.352 \cdot 10^{-3}$	$8.905 \cdot 10^{-5}$	$1.093 \cdot 10^{-3}$	$1.093 \cdot 10^{-3}$
65	11	$1.223 \cdot 10^{-3}$	$7.348 \cdot 10^{-4}$	$6.796 \cdot 10^{-3}$	$2.744 \cdot 10^{-3}$
66	11	$7.361 \cdot 10^{-4}$	$2.644 \cdot 10^{-4}$	$1.007 \cdot 10^{-3}$	$1.007 \cdot 10^{-3}$
67	13	$4.534 \cdot 10^{-3}$	$2.767 \cdot 10^{-3}$	$7.778 \cdot 10^{-5}$	$7.778 \cdot 10^{-5}$
68	17	$1.255 \cdot 10^{-4}$	$1.326 \cdot 10^{-4}$	$1.358 \cdot 10^{-4}$	$1.240 \cdot 10^{-4}$
69	17	$3.637 \cdot 10^{-5}$	$2.523 \cdot 10^{-5}$	$4.649 \cdot 10^{-5}$	$3.564 \cdot 10^{-5}$
70	19	$3.198 \cdot 10^{-5}$	$4.131 \cdot 10^{-6}$	$4.826 \cdot 10^{-6}$	$4.826 \cdot 10^{-6}$
71	13	$1.663 \cdot 10^{-5}$	$8.928 \cdot 10^{-6}$	$4.804 \cdot 10^{-5}$	$8.453 \cdot 10^{-5}$
72	17	$3.503 \cdot 10^{-1}$	$2.582 \cdot 10^{-1}$	$7.481 \cdot 10^{-1}$	$4.527 \cdot 10^{-1}$
73	17	$8.724 \cdot 10^{-2}$	$4.419 \cdot 10^{-2}$	$1.796 \cdot 10^{-3}$	$1.886 \cdot 10^{-2}$
74	17	$3.184 \cdot 10^{-2}$	$1.210 \cdot 10^{-2}$	$7.433 \cdot 10^{-4}$	$7.433 \cdot 10^{-4}$
75	17	$3.811 \cdot 10^{-2}$	$1.064 \cdot 10^{-2}$	$1.160 \cdot 10^{-3}$	$1.160 \cdot 10^{-3}$
76	17	$4.177 \cdot 10^{-2}$	$4.106 \cdot 10^{-2}$	$1.565 \cdot 10^{-1}$	$7.007 \cdot 10^{-2}$
77	17	$1.869 \cdot 10^{-2}$	$1.035 \cdot 10^{-2}$	$3.651 \cdot 10^{-1}$	$9.428 \cdot 10^{-2}$
78	17	$8.984 \cdot 10^{-3}$	$2.718 \cdot 10^{-3}$	$1.120 \cdot 10^{-3}$	$2.695 \cdot 10^{-2}$
79	12	$2.253 \cdot 10^{+3}$	$8.890 \cdot 10^{+2}$	$2.331 \cdot 10^{+1}$	$7.772 \cdot 10^{+3}$
80	8	$8.252 \cdot 10^{-5}$	$6.264 \cdot 10^{-5}$	$2.702 \cdot 10^{-3}$	$6.386 \cdot 10^{-5}$
81	8	$5.410 \cdot 10^{-5}$	$5.416 \cdot 10^{-5}$	$1.001 \cdot 10^{-3}$	$3.628 \cdot 10^{-5}$
82	8	$2.502 \cdot 10^{-4}$	$3.229 \cdot 10^{-4}$	$9.964 \cdot 10^{-3}$	$2.574 \cdot 10^{-4}$

TABLE II

(*Continued*)

No.	N	Eq. (*11*)	Eq. (*12*)	Eq. (*13*)	Eq. (*14*)
83	8	$5 \cdot 398 \cdot 10^{-4}$	$5 \cdot 355 \cdot 10^{-4}$	$1 \cdot 813 \cdot 10^{-2}$	$4 \cdot 870 \cdot 10^{-4}$
84	8	$4 \cdot 726 \cdot 10^{-5}$	$5 \cdot 309 \cdot 10^{-5}$	$4 \cdot 036 \cdot 10^{-4}$	$4 \cdot 838 \cdot 10^{-5}$
85	8	$4 \cdot 744 \cdot 10^{-7}$	$2 \cdot 971 \cdot 10^{-7}$	$9 \cdot 518 \cdot 10^{-8}$	$5 \cdot 178 \cdot 10^{-7}$
86	8	$3 \cdot 930 \cdot 10^{-4}$	$1 \cdot 961 \cdot 10^{-4}$	$1 \cdot 508 \cdot 10^{-4}$	$4 \cdot 908 \cdot 10^{-4}$
87	8	$4 \cdot 822 \cdot 10^{-6}$	$3 \cdot 315 \cdot 10^{-6}$	$4 \cdot 520 \cdot 10^{-6}$	$1 \cdot 226 \cdot 10^{-5}$
88	8	$2 \cdot 104 \cdot 10^{-6}$	$1 \cdot 848 \cdot 10^{-6}$	$1 \cdot 424 \cdot 10^{-6}$	$1 \cdot 983 \cdot 10^{-6}$
89	11	$8 \cdot 202 \cdot 10^{-3}$	$4 \cdot 627 \cdot 10^{-3}$	$1 \cdot 191 \cdot 10^{-2}$	$6 \cdot 460 \cdot 10^{-3}$
80	11	$5 \cdot 607 \cdot 10^{-4}$	$2 \cdot 328 \cdot 10^{-4}$	$6 \cdot 077 \cdot 10^{-3}$	$6 \cdot 601 \cdot 10^{-4}$
91	13	$4 \cdot 788 \cdot 10^{-1}$	$2 \cdot 386 \cdot 10^{-1}$	$2 \cdot 737 \cdot 10^{-2}$	$2 \cdot 737 \cdot 10^{-2}$
92	13	$4 \cdot 602 \cdot 10^{-1}$	$2 \cdot 334 \cdot 10^{-1}$	$1 \cdot 875 \cdot 10^{-2}$	$1 \cdot 875 \cdot 10^{-2}$
93	13	$4 \cdot 881 \cdot 10^{-1}$	$2 \cdot 366 \cdot 10^{-1}$	$2 \cdot 766 \cdot 10^{-2}$	$2 \cdot 766 \cdot 10^{-2}$
94	13	$4 \cdot 768 \cdot 10^{-1}$	$2 \cdot 233 \cdot 10^{-1}$	$3 \cdot 353 \cdot 10^{-2}$	$3 \cdot 353 \cdot 10^{-2}$
95	17	$9 \cdot 486 \cdot 10^{-3}$	$8 \cdot 459 \cdot 10^{-3}$	$1 \cdot 496 \cdot 10^{-1}$	$7 \cdot 140 \cdot 10^{-2}$
96	14	$1 \cdot 247 \cdot 10^{-1}$	$2 \cdot 105 \cdot 10^{-2}$	$5 \cdot 740 \cdot 10^{-1}$	$2 \cdot 794 \cdot 10^{-1}$
97	16	$1 \cdot 639 \cdot 10^{-3}$	$1 \cdot 639 \cdot 10^{-3}$	$5 \cdot 273 \cdot 10^{-3}$	$5 \cdot 263 \cdot 10^{-3}$
98	16	$1 \cdot 529 \cdot 10^{-3}$	$1 \cdot 647 \cdot 10^{-3}$	$3 \cdot 797 \cdot 10^{-2}$	$2 \cdot 464 \cdot 10^{-3}$
99	10	$6 \cdot 710 \cdot 10^{-1}$	$6 \cdot 254 \cdot 10^{-1}$	$7 \cdot 382 \cdot 10^{-1}$	$7 \cdot 417 \cdot 10^{-1}$
100	10	$1 \cdot 386 \cdot 10^{-2}$	$2 \cdot 690 \cdot 10^{-3}$	$1 \cdot 404 \cdot 10^{-2}$	$1 \cdot 404 \cdot 10^{-2}$
101	10	$6 \cdot 253 \cdot 10^{0}$	$6 \cdot 444 \cdot 10^{0}$	$6 \cdot 497 \cdot 10^{0}$	$6 \cdot 487 \cdot 10^{0}$
100	10	$1 \cdot 386 \cdot 10^{-2}$	$2 \cdot 690 \cdot 10^{-3}$	$1 \cdot 404 \cdot 10^{-2}$	$1 \cdot 404 \cdot 10^{-2}$
102	10	$9 \cdot 355 \cdot 10^{-2}$	$7 \cdot 870 \cdot 10^{-2}$	$6 \cdot 103 \cdot 10^{-2}$	$4 \cdot 817 \cdot 10^{-2}$
103	10	$8 \cdot 935 \cdot 10^{-3}$	$3 \cdot 724 \cdot 10^{-3}$	$1 \cdot 061 \cdot 10^{-2}$	$1 \cdot 061 \cdot 10^{-2}$
104	10	$4 \cdot 127 \cdot 10^{-4}$	$4 \cdot 934 \cdot 10^{-4}$	$1 \cdot 531 \cdot 10^{-2}$	$1 \cdot 943 \cdot 10^{-3}$
105	11	$1 \cdot 003 \cdot 10^{-4}$	$1 \cdot 117 \cdot 10^{-4}$	$7 \cdot 326 \cdot 10^{-4}$	$6 \cdot 869 \cdot 10^{-5}$
106	11	$1 \cdot 048 \cdot 10^{-2}$	$1 \cdot 151 \cdot 10^{-2}$	$1 \cdot 566 \cdot 10^{-2}$	$1 \cdot 081 \cdot 10^{-2}$
107	11	$1 \cdot 024 \cdot 10^{-1}$	$1 \cdot 148 \cdot 10^{-1}$	$1 \cdot 084 \cdot 10^{-1}$	$1 \cdot 255 \cdot 10^{-1}$
108	10	$4 \cdot 428 \cdot 10^{-1}$	$4 \cdot 168 \cdot 10^{-1}$	$4 \cdot 950 \cdot 10^{-1}$	$4 \cdot 888 \cdot 10^{-1}$
109	10	$4 \cdot 443 \cdot 10^{-2}$	$3 \cdot 624 \cdot 10^{-2}$	$3 \cdot 650 \cdot 10^{-2}$	$3 \cdot 650 \cdot 10^{-2}$
110	10	$7 \cdot 975 \cdot 10^{0}$	$7 \cdot 420 \cdot 10^{0}$	$7 \cdot 742 \cdot 10^{0}$	$7 \cdot 742 \cdot 10^{0}$
111	13	$3 \cdot 806 \cdot 10^{2}$	$8 \cdot 171 \cdot 10^{1}$	$3 \cdot 000 \cdot 10^{0}$	$3 \cdot 000 \cdot 10^{0}$
112	11	$1 \cdot 832 \cdot \cdot 10^{1}$	$5 \cdot 047 \cdot 10^{0}$	$2 \cdot 975 \cdot 10^{1}$	$2 \cdot 975 \cdot 10^{1}$
113	12	$3 \cdot 845 \cdot 10^{-3}$	$2 \cdot 479 \cdot 10^{-3}$	$1 \cdot 340 \cdot 10^{-1}$	$3 \cdot 591 \cdot 10^{-2}$
114	12	$4 \cdot 904 \cdot 10^{-3}$	$2 \cdot 181 \cdot 10^{-3}$	$4 \cdot 881 \cdot 10^{-3}$	$4 \cdot 881 \cdot 10^{-3}$
115	11	$1 \cdot 958 \cdot 10^{0}$	$4 \cdot 074 \cdot 10^{-1}$	$2 \cdot 195 \cdot 10^{-2}$	$2 \cdot 195 \cdot 10^{-2}$

the experimental error), hence the way of description of the additional Gibbs function is irrelevant. As the non-ideality of behaviour of a mixture is predominantly due to mutual specific interactions of the solvent and solute molecules (formation of hy-

TABLE III

Criteria of the Friedman test and average orders of the model equations (*11*) through (*14*) for the individual data types in binary mixtures

Data type	Q	Q_{crit}[a]	$\bar{R}$			
			Eq. (*11*)	Eq. (*12*)	Eq. (*13*)	Eq. (*14*)
pK	15·00	7·77	2·63	1·73	2·93	2·70
IR	16·64	7·76	2·88	1·60	2·86	2·66
UV-VIS	12·59	7·74	3·00	1·77	2·89	2·34
NMR	1·32	7·67	2·70	2·10	2·60	2·60
log k	3·48	7·67	2·70	2·00	3·00	2·30

[a] See ref.[105], significance level $\alpha = 0.05$.

drogen bonds, CT complexes etc.), the conclusions following from Table III agree — in principle — with the ideas about the mechanism of action of solvents in various processes.

The average mean square determined from the mean squares of the regression model (*12*) applied to logarithms of dissociation constants (in the form of pK) has the value of $5.79 \cdot 10^{-2}$. Hence the average standard deviation is 0·24, which is roughly 2−3 times more than the experimental error in the pK values determined in organic solvents. Although this relation is practically acceptable, it indicates the existence of a non-described behaviour in the system dissociation process – binary solvent. The average mean square determined for log k has the value of $9.70 \cdot 10^{-2}$, which gives the average standard deviation value of 0·31. Also in this case, a part of experimental variability remains unexplained.

From the technical point of view, all the regression models used are well-converging; out of the four-parameter equations (Eqs (*11*), (*13*), and (*14*)), the best--ballanced results are obtained from the 3rd order model by Margules (Eq. (*11*)) which also shows the fastest convergence at the minimum intercorrelation of parameters. The parameters in Eqs (*10*) through (*12*) can advantageously be calculated by means of multiple linear regression.

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